PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 51/41, C08K 5/098	A1	(11) International Publication Number: WO 99/10307 (43) International Publication Date: 4 March 1999 (04.03.99)

(21) International Application Number: PCT/US98/17488

(22) International Filing Date: 24 August 1998 (24.08.98)

(30) Priority Data:
08/918,488 26 August 1997 (26.08.97) US

(71) Applicant: OMG AMERICAS, INC. [US/US]; 811 Sharon Drive, Westlake, OH 44145 (US).

(72) Inventors: KHATTAR, Rajesh; 330 Manchester Court, Richmond Heights, OH 44143 (US). LABOVITZ, Benjamin, Paul; 2172 Rexwood Road, Cleveland Heights, OH 44118 (US). BAKER, Paulette; 17340 Haskins Road, Chagrin Falls, OH 44023 (US).

(74) Agents: JOSEPHIC, David, J. et al.; Wood, Herron & Evans, L.L.P., 2700 Carew Tower, Cincinnati, OH 45202 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS FOR IMPROVING SHELF STABILITY OF LIQUID OVERBASED CALCIUM CARBOXYLATES, MIXED METAL STABILIZERS CONTAINING SAME, AND STABILIZING HALOGEN-CONTAINING POLYMERS THEREWITH

(57) Abstract

Shelf stable liquid overbased calcium carboxylates are prepared by reacting a calcium base with a monocarboxylic acid, and carbonating in the presence of a promoter mixture with a phenol and an alcohol under controlled temperature conditions, to produce shelf stable liquids. Mixed metal stabilizer compositions are prepared by blending the stable liquid calcium carboxylate with a metal carboxylate of zinc, cadmium or tin. The mixed metal carboxylates are also shelf stable and are used for stabilizing halogen-containing polymers to provide heat stability, clarity and improved plate out properties.

PROCESS FOR IMPROVING SHELF STABILITY OF LIQUID OVERBASED CALCIUM CARBOXYLATES, MIXED METAL STABILIZERS CONTAINING SAME, AND STABILIZING HALOGEN-CONTAINING POLYMERS THEREWITH

FIELD OF THE INVENTION

The present invention relates to a process for producing shelf stable liquid overbased calcium carboxylates and mixed metal stabilizers containing the overbased calcium carboxylate and a metal carboxylate of zinc, cadmium or tin. The shelf stable mixed metal stabilizer compositions are used as stabilizers for halogen-containing polymers such as polyvinyl chloride (PVC).

BACKGROUND OF THE INVENTION

The preparation of overbased calcium or barium salts of carboxylic acids, alkyl phenols, and sulfonic acids are disclosed in the following U. S. Patents: 2,616,904; 2,760,970; 2,767,164; 2,798,852; 2,802,816; 3,027,325; 3,031,284; 3,342,733; 3,533,975; 3,773,664; and 3,779,922. The use of these overbased metal salts in the halogen-containing organic polymer is described in the following U S. Patents:

permanent damage to the eye. Furthermore, propylene oxide is extremely flammable and explosive in nature under certain conditions. Propylene oxide boils at 94° F and flashes at -20° F. As a result, extreme precautions are required to handle propylene oxide at the plant site. Special storage equipment is required for propylene oxide and other safety features are necessary. U. S. Patent No. 4,665,117 describes the use of propylene oxide at 150° C. At this temperature, propylene oxide will be in the gaseous phase. Under these operating conditions, more than stoichiometric amounts of propylene oxide are required to carry the reaction to completion because propylene oxide will escape from the reaction mixture and this requires additional handling of the excess propylene oxide.

With the movement in the plastics industry to remove heavy metals, liquid calcium-zinc stabilizers are desirous, but not practical, as replacements for barium-cadmium or barium-zinc. Low metal concentrations, poor compatibility, haziness in clear products and plate out during processing in PVC have severely limited the universal acceptance of calcium based liquid stabilizer compositions. Problems are encountered in the stability of these compositions upon standing or storage. Storage stability is due to the incompatibility among the metal salts employed in the composition and is exhibited by increased turbidity, viscosity, or insoluble solids over time. As a result, the liquid calcium compositions are no longer homogeneous or readily pourable and must be specially treated in order to be used. U. S. Patent No. 5,322,872 is directed to stabilized compositions

temperature conditions of the reaction mixture must be controlled up to a temperature of about 80° C, preferably in the range of about 15° C to about 80° C, to produce a stable liquid. Above about 80° C, the reaction stalls and the desired stable liquid product is not obtained. Thereafter, the stable liquid is added to a metal soap stabilizer selected from the group of zinc, cadmium and tin carboxylates to provide a shelf stable mixed metal stabilizer composition.

The liquid overbased calcium carboxylate/carbonate may be first treated with an organic phosphite to react with any phenolic color-producing component to improve its color as disclosed in United States Application Serial No. 08/744,642, filed November 6, 1996, and this application in its entirety is incorporated herein by reference. As disclosed in that patent application, organic phosphites suitable for use include various diorganic phosphites and triorganic phosphites to react with color species which may be produced by or in conjunction with the phenol.

A number of benefits are obtained by the inventive process over the prior art methods. Improvements in shelf stability of liquid overbased calcium carboxylates are achieved. Also, shelf stable mixed metal stabilizer systems of an overbased calcium carboxylate/carbonate and metal soap stabilizers are obtained. For example, enhanced shelf stability for the liquid overbased calcium carboxylates and mixed metal stabilizer compositions of this invention have been demonstrated over presently commercially available products. Whereas, in contrast, presently available

More generally, the process of the present invention for improving the stability of basic calcium carboxylates and mixed metal stabilizers comprises the steps of (A) preparing, in the absence of free oxygen, a mixture comprising a calcium metal base, at least one monocarboxylic acid, and a phenolic/alcohol promoter mixture to facilitate the incorporation of the calcium into the overbased carboxylate, and the ratio of equivalents of the calcium base to the combination of the other components being greater than 1:1, (B) treating said mixture with an acidic gas in the absence of free oxygen until the titratable basicity (phenolphthalein indicator) of the mixture has been substantially reduced, and (C) treating the reaction mixture containing the basic calcium organic salt with an organic phosphite which reacts with the color-producing component present in the final mixture. It is preferred that the entire process involving steps (A), (B) and (C) be conducted in the absence of free oxygen since the presence of oxygen or oxidizing agents results in more highly colored product. Generally, the process is conducted in an atmosphere of nitrogen.

The most critical features of the method include the use of a phenol or alkyl phenol and alcohol as the carbonation aid or promoter. Furthermore, the temperatures of the reaction must be controlled up to about 80° C, preferably in the ranges of about 15° C to about 80° C. It has been unexpectedly found that stable liquid overbased calcium carboxylates can be produced by this method. Moreover, these liquids are compatible

the organic moiety. The basic metal salts often have been referred to in the art as "overbased" or superbased" to indicate the presence of an excess of the basic component.

The calcium metal base is utilized in the process and may be derived from any of the alkaline earth metals. The calcium metal bases include the metal oxides and hydroxides, and in some instances, the sulfides, hydrosulfides, etc. In addition to the calcium metal base, the reaction mixture contains at least one monocarboxylic acid. The monocarboxylic acids may be aliphatic or aromatic monocarboxylic acids or mixtures thereof. Among the aliphatic monocarboxylic acids which can be utilized in the present invention are the aliphatic monocarboxylic acids containing an average of at least about 6 carbon atoms and more generally an average of from about 6 to about 30 carbon atoms. The mixture useful in step (A) contains at least one phenol, preferably an alkyl phenol, and an aliphatic alcohol which serve as promoters in the overall process. The alkyl phenols preferably include dodecylphenol and nonylphenol. The alcohols which are useful as promoters include any one of the various available substituted or unsubstituted aliphatic or cycloaliphatic alcohols containing from 1 to about 20 or more carbon atoms. The amounts of the phenol and alcohol included in the mixture as promoters are not critical. The promoters are included in the mixture to contribute to the utilization of the acidic gas during treatment of the mixture with the acidic gas. Generally, at least about 0.1 equivalent and preferably from about 0.05 to about 1.5

be greater than 1:1 in order to provide a basic product. More generally, the ratio of equivalents will be at least 3:1.

The step of the process (B) involves treating the mixtures described above with an acidic gas in the absence of free oxygen until the titratable basicity is determined using a phenolphthalein. Generally, the titratable basicity is reduced to a base number below about 10. The first two steps of the process of the present invention require low temperature operating conditions and preferably the exclusion of free oxygen. The ingredients in step (A) are mixed, heated to a low temperature of about 15° C to about 80° C, and then treated with the acidic gas. After carbonation, and the mixture may be heated to a temperature of about 120-125° C which is sufficient to drive off water and alcohol contained in the mixture. The treatment of the mixture with the acidic gas preferably is conducted at low temperatures, and the range of temperatures used for this step may be any temperature above ambient temperature up to about 150° C, and more preferably from a temperature of about 15° C to about 80° C. By the term "acidic gas" as used in this specification and in the claims is meant a gas which upon reaction with water will produce an acid. Thus, such gases as sulfur dioxide, sulfur trioxide, carbon dioxide, carbon disulfide, hydrogen sulfide, etc., are exemplary of the acidic gases which are useful in the process of this invention. Of these acids, sulfur dioxide and carbon dioxide are preferred, and the most preferred is carbon dioxide.

limitation, the organic phosphites may be generally characterized by the formula

$$R_1O{-}\underset{\displaystyle OR_3}{\underset{|}{P}}{-}OR_2$$

in which R_1, R_2 and R_3 are hydrogen, alkyl, alkenyl, aryl, alkaryl, aralkyl and cycloalkyl radicals or groups, and substituted derivatives thereof. Thus, triphosphites and diphosphites are suitable including trialkyl or dialkyl phosphites, for example, having from about 1 to 18 carbon atoms. Specific examples of organic phosphites, including the preferred liquid organic phosphites, are tributyl phosphite, triisooctyl phosphite and triisodecyl phosphite, diisooctyl phosphite, dibutyl phosphite and tetrakis isodecyl 4,4-isopropylidene diphosphite, diphenyl isodecyl phosphite, phenyl neopentylene glycol phosphite, diphenyl phosphite, triphenyl phosphite, phenyl diisodecyl phosphite and poly(dipropyleneglycol phenyl phosphite. Other organic phosphites may be used in view of this description and exemplification. The amounts of the organic phosphites suitable for use in the treatment are sufficient to inhibit or destroy the color-producing body. More specifically, a molar ratio of phenol to organic phosphite should be between about 0.5-2:1 in order to substantially completely inhibit or destroy the color-producing body.

E. <u>Halogen-Containing Polymer</u>

A halogen-containing polymer, such as a vinyl halide resin, most commonly stabilized with the basic metal salts of this invention is

such as beta-diketones, phosphite and phenolic antioxidants have been employed in the following examples to illustrate the practice of this invention. The following examples illustrate the preparation of the basic calcium carboxylate/carbonate salts in accordance with the method of the present invention, but these examples are not considered to be limiting the scope of this invention. Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, and all temperatures are in degrees centigrade.

PREPARATION OF STABLE LIQUID OVERBASED CALCIUM CARBOXYLATE

Example 1

Charge mineral oil (290 gm), oleic acid (186 gm), butanol (64 gm), methanol (64 gm), amyl alcohol (64 gm), dodecyl phenol (70 gm), water (19 gm) and calcium hydroxide (243 gm). Start mixing and make sure that all calcium hydroxide is mixed and does not clump up or stick to the bottom of the reactor. Start carbon dioxide sparge, set the flow meter at 3 SCFH. Set the temperature to 40° C, watch the reaction closely, take sample every 0.5 hour and centrifuge. After the carbonation is complete, heat the reation to 120-125° C over a period of 1 hour. Remove all the distillates from the reaction. Once all the water has been removed, filter the product. The resulting filtered product is a pale brown viscous product containing 13-14% calcium.

The following Table I summarizes the results:

Table I

	1 Day	2 Days	7 Days	9 Days	16 Days
Stabilizer containing New Calcium	5.5	5.2	5.1	4.9	4.4
Stabilizer containing Old Calcium	>200	>200	>200	>200	>200

Turbidity readings were measured in JTU. The turbidity observation between 1-30 indicates that the product is free from haze, and the observation above 200 JTU indicates that the product is hazy in nature. If the turbidity observation stays constant over a period of time, this means that the product possesses good shelf stability. This means that the product does not pick up any haze or undergo change in physical appearance over a period of time.

The data of Table I shows that the New Calcium possessed good shelf stability over a 2-week period, whereas the commercially available Old Calcium is hazy in nature.

<u>Shelf Stability of Mixed Metal Stabilizer of Overbased Calcium Carboxylate/Carbonate and Zinc Carboxylate (Calcium/Zinc Stabilizer)</u>

Shelf stability of mixed metal calcium/zinc stabilizers containing New Calcium (Example 1) and Old Calcium was also monitored over a period of two weeks as shown in Table II. The stabilizer formulation contained 5% Ca, 1.2% Zn (zinc octoate), 3.5% P (diphenyl isodecyl phosphite), 5% carboxylic acid (oleic acid),3% anti-oxidant, 3% β-diketone (dibenzoyl methane) and diluent.

<u>Shelf Stability of Mixed Metal Overbased Calcium/Cadmium Carboxylate Stabilizers (Calcium/Cadmium Stabilizer)</u>

Shelf stability of a calcium/cadmium stabilizer containing New Calcium (Example 1) and Old Calcium was also monitored over a period of two weeks as shown in Table IV. Stabilizer formation contained 5% Ca, 1.5% Cd (cadmium octoate), 3% P (diphenyl decyl phosphite), 5% carboxylic acid (oleic acid), 2% anti-oxidant (bisphenol-A), 3% β-diketone (dibenzoyl methane) and diluent.

Table IV

	0 Days	1 Day	3 Days	4 Days	7 Days	14 Days
Stabilizer containing New Calcium	17	29	23	19	16	16
Stabilizer containing Old Calcium	>200	>200	>200	>200	>200	>200

The data illustrates that the incorporation of New Calcium, versus Old Calcium, makes the stabilizer shelf stable.

<u>Shelf Stability of Mixed Metal Overbased Calcium/Tin Carboxylate Stabilizers (Calcium/Tin Stabilizer)</u>

Shelf stability of a calcium/tin stabilizer containing New Calcium (Example 1) and Old Calcium was also monitored over a period of two weeks as shown in Table V. Stabilizer formulation contained 5% Ca, 1.5% Sn (tin maleate), 3% P (diphenyl decyl phosphite), 5% carboxylic acid (oleic acid), 2% anti-oxidant (bisphenol-A), 3% β-diketone (dibenzoyl methane) and diluent.

375° F over 56 minutes. Yellowness [+b chromaticity of CIELAB color space (Commission Internationale de l'Eclairage) developed in 1976] was measured with a Minolta colorimeter. The values of the rate of thermal degradation are shown in the following Table VI.

The PVC formulation containing the stabilizer with the New Calcium (A) develops color at a slower rate than the PVC formulation using the stabilizer with the Old Calcium (B).

Table VI

Time (minutes)	New Calcium A	Old Calcium B
7	10.51	10.3
14	11.28	11.35
21	12.57	12.51
28	16.29	16.1
35	19.5	27.6
42	38.26	52.83
49	44.77	61.28
56	63.97	69.38

<u>Performance Comparisons: Clarity</u>

The New Calcium (Example 1) and Old Calcium were incorporated into mixed metal stabilizer compositions for the purpose of observing their influence on the clarity of the PVC application. The stabilizer compositions are as follows:

B and C with A containing the New Calcium, B containing the Old Calcium and C containing the non-carbonated calcium carboxylate.

Plate out is determined by introducing a red pigment into a PVC formulation containing the stabilizer and allowing the pigment to migrate from the formulation to the metal rolls of a two roll mill at 340° F. A white clean up compound is then placed onto the rolls and the degree of plate out is determined by the amount of red picked up by the clean up compound. The colorimeter assigns a numerical value on the CIElab scale for the degree of redness or plate out (+a).

Red pigmented formulation:	Clean Up Compound
100 PVC resin	100 PVC resin
40 phthalate plasticizer	40 phthalate plasticizer
8 epoxidized soybean oil	8 epoxidized soybean oil
0.2 stearic acid	0.2 stearic acid
2 red 2B pigment	4 Titanium dioxide
1.5 stabilizer variable	3 lead phosphite

The red formulation is milled for 4 minutes undisturbed after which the clean up compound is introduced and milled for three minutes undisturbed.

Colorimeter readings, +a value indicating increasing degree of red:

A - 3.34

B - 3.64

C +21.0

There is essentially no difference between the New and Old Calcium as far as plate out resistance. However, there is a significant

CLAIMS:

1. A process for making a shelf stable liquid of an overbased calcium carboxylate comprising

preparing an overbased calcium carboxylate/carbonate by reacting a calcium base with a monocarboxylic acid and carbonating in the presence of a promoter mixture of a phenol and an alcohol,

conducting the reaction under a controlled temperature up to about 80° C to produce a shelf stable liquid.

8. The process of claim 1 wherein said phenol is an alkyl phenol.

9. The process of claim 1 wherein said phenol is selected from the group consisting of dodecylphenol and nonylphenol.

10. The process of claim 1 which comprises the further step of adding a metal carboxylate is selected from the group consisting of zinc, cadmium and tin carboxylate to make a shelf stable mixed metal stabilizer composition.

11. The shelf stable liquid overbased calcium carboxylate/carbonate prepared in accordance with the process of claim 1.

12. The shelf stable liquid overbased calcium carboxylate/carbonate prepared in accordance with the process of claim 2.

13. The shelf stable liquid overbased calcium carboxylate/carbonate prepared in accordance with the process of claim 7.

14. The shelf stable liquid overbased calcium carboxylate/carbonate prepared in accordance with the process of claim 8.

21. A halogen-containing polymer composition comprising a halogen-containing polymer and a heat stabilizing amount of the composition of claim 15.

22. A halogen-containing polymer composition comprising a halogen-containing polymer and a heat stabilizing amount of the composition of claim 16.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/17488

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9717400 A	15-05-1997	AU 7674096 A	29-05-1997
		EP 0859812 A	26-08-1998

Form PCT/ISA/210 (patent family annex) (July 1992)